indicate that $(C_2H_5)_3SnH$ should react with $SeCl_4$, $TeCl_4$, $RuCl_2$ or K_2OsCl_6 to yield $(C_2H_5)_3SnCl$ and the free elements Se, Te, Ru and Os.

Apparently $(C_2H_5)_3SnH$ is more reactive than $(C_2H_5)_3GeH$[1] is, since the latter reacts comparatively slowly with the oxygen in the air, and not at all with $CdCl_2$ or CH_3COOH. Oxygen in the air reacts more rapidly with the organotin hydride $2(C_2H_5)_3SnH + O_2 \rightarrow 2(C_2H_5)_3SnOH$ followed by loss of water at elevated temperature (if such be available) $2(C_2H_5)_3SnOH \rightarrow [(C_2H_5)_3Sn]_2O + H_2O \uparrow$. Acetic acid reacts rapidly in reflux $(C_2H_5)_3SnH + CH_3COOH \rightarrow (C_2H_5)_3SnOCOCH_3 + H_2$.

Experimental

Equipment as before[1] included distilling units with ground joints, also transfer micropipets, a pycnometer for density and some very small distilling units.

Triethyltin Hydride.—This compound reacts with the oxygen in air, and therefore a minimum amount of air should be present during the preparation of the compound. Gradual addition of 133 g. of $(C_2H_5)_3SnI$ over 15 min. to a solution of 18 g. of $LiAlH_4$ in 200 ml. of dry ether was followed by 90 minutes of reflux. After slow addition of water until there were two layers, there followed slow addition of a *slight deficiency* of 6 *M* H_2SO_4, then shaking and separation of layers soon. Next came drying with Na_2SO_4 in a closed container, followed by filtration and then distillation of the ether. A first fractional distillation under 47 mm. pressure furnished 40 g. of crude $(C_2H_5)_3SnH$ boiling at approximately 70° and left 42 g. of crude $[(C_2H_5)_3Sn]_2O$ in the residue; redistillation of the $(C_2H_5)_3SnH$ furnished a center fraction boiling at 69–70° under 47 mm. pressure, later used in all measurements. An actual yield of 48% as $(C_2H_5)_3SnH$ might have been higher in the absence of oxygen, which caused formation of some $[(C_2H_5)_3Sn]_2O$. All samples were stored in sealed tubes with a minimum amount of air present; upon standing one month some samples developed a little pressure, but no metallic tin formed. At first $(C_2H_5)_3SnH$ had the b.p. 146° under 760 mm. pressure, but the b.p. in air rose to 149° within one minute of reflux and the inoffensive odor of pure $(C_2H_5)_3SnH$ changed in part to the disagreeable odor of $[(C_2H_5)_3Sn]_2O$. *Anal.* Calcd. for $(C_2H_5)_3SnH$: mol. wt., 206.9; Sn, 57.5; hydride H, 0.49. Found: mol. wt. (naphthalene), 223; Sn, 57.1; hydride H, 0.49. Found: mol. wt. (naphthalene), 223; Sn, 57.1; hydride H, 0.49. Also, pure $(C_2H_5)_3SnH$ had a weak, inoffensive odor, $d^{20}{}_4$ 1.259 and n^{20} 1.472_5. Determination of hydride hydrogen employed a gentle 3 minute reflux with excess glacial acetic acid followed by collection and measurement of the volume of hydrogen in the gas buret, after the return of the system to room temperature with much agitation to ensure saturation of the gas with water vapor; the equation is at the end of the Discussion. This analytical data and the 25 reactions in Table I support the formula $(C_2H_5)_3SnH$.

Starting materials other than commercial products included anhydrous $CdCl_2$ and $SnCl_2$ made from commercial hydrates, and included special preparations of $GeCl_4$, $VOCl_3$ and CrO_2Cl_2. All the solids were dry and powdered.

Reactions of $(C_2H_5)_3SnH$.—These had some alterations on the methods used with $(C_2H_5)_3GeH$.[1] Slow reactions of $(C_2H_5)_3SnH$ in reflux with ZnO, Fe_2O_3, PbO and As_4O_6 permitted addition of the hydride to the inorganic oxide. Gradual addition of the inorganic halide or HgO was necessary in 14 instances. Powdered $KMnO_4$ reacted satisfactorily with $(C_2H_5)_3SnH$ in the absence of a solvent to furnish a yield of $[(C_2H_5)_3Sn]_2O$ superior to that obtained with $(C_2H_5)_3GeH$ in acetone.[1] Table I lists the individual reactions, with yields based upon the starting material present in the lesser amount.

Identification of the Chief Organotin Product in Table I.—This follows the separative methods for the products from $(C_2H_5)_3GeH$.[1] Usually a first fractional distillation separated the chief organotin product from excess $(C_2H_5)_3SnH$, while a second or third fractional distillation produced a sufficiently pure fraction of the chief organotin compound to allow determination of the boiling point and refractive index. Volumes, boiling points and refractive indices of the various liquid fractions established the identities and amounts of the compounds present. Accepted b.p.'s and refractive indices follow: $(C_2H_5)_3SnCl$, b.p. 210°, n^{20} 1.507; $(C_2H_5)_3SnBr$, b.p. 224°, n^{20} 1.5281; $[(C_2H_5)_3Sn]_2O$, b.p. 272°.[8] Recent unpublished measurements by the present author furnished $d^{20}{}_4$ 1.401 and n^{20} 1.501_0 for center-fraction $[(C_2H_5)_3Sn]_2O$.

Identification of Other Products in Table I.—Visual observations sufficed to establish the formation of the metals and also the condensation of a little water. Other tests included the insolubility in water, the inflammability of hydrogen, colors, the odor of hydrogen sulfide, the colors of the vanadium compounds obtained upon dissolving in hydrochloric acid, or the burning of the exit gas to deposit a small amount of brownish germanium.

[8] E. Krause and A. V. Grosse, "Die Chemie der metall-organischen Verbindungen," Photolithoprint, Edwards Bros., Ann Arbor, Mich., 1943, pp. 327, 336, 743.

PHILADELPHIA 4, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY OF THE UNIVERSITY OF TEXAS]

Some Compressibility Relations of 1,2-Dichloro-1,1-difluoroethane

BY MARVIN LEE DEVINEY, JR.,[1] WITH W. A. FELSING[2]

RECEIVED APRIL 3, 1957

Compressibility data for liquid 1,2-dichloro-1,1-difluoroethane in the range 80 to 225° are given. Vapor pressures are given both in equation form and tabular form for the range 110 to 220°.

Introduction

Compressibility data on numerous hydrocarbons have been determined in and presented[3] from this Laboratory but this investigation is the first dealing with the compressibilities of a halogenated hydrocarbon. 1,2-Dichloro-1,1-difluoroethane may prove useful in refrigeration and air-conditioning applications.

Previous Investigations.—No previous compressibility data for this compound have been found in the literature. Henne and Hubbard[4] have reported data on the freezing point, the boiling point, the density at 20° and the refractive index. Harmon[5] presented boiling point and refractive index data. However, pressure–volume–temperature relations have been reported by Benning and McHarness[6] on four similar halogenated com-

(1) Special Problems Laboratory, Chemcel Plant, Celanese Corporation of America, Bishop, Texas.

(2) Deceased, October 5, 1952.

(3) H. O. Day with W. A. Felsing, THIS JOURNAL, **74**, 1951 (1952); ref. 1.

(4) A. L. Henne and D. M. Hubbard, *ibid.*, **58**, 404 (1936).

(5) Jesse Harmon, U. S. Patent 2,399,024 (April 23, 1946).

(6) A. F. Benning and R. C. McHarness, *Ind. Eng. Chem.*, **32** 698 (1940)

pounds: chlorodifluoromethane, dichlorofluoromethane, trichlorofluoromethane and 1,1,2-trichloro-1,2,2-trifluoroethane.

Experimental

Method and Apparatus.—The apparatus used for the compressibility measurements has been described previously by Kelso and Felsing.[7] Bath temperatures were held constant to ±0.005° by means of a platinum resistance thermometer in conjunction with a Mueller bridge and a photoelectric cell relay system. The regulating platinum resistance thermometer, calibrated by the National Bureau of Standards, also determined the thermostat temperature. The samples of liquid 1,2-dichloro-1,1-difluoroethane of various sizes were introduced into glass liners (for the pressure bomb) by distillation under a high vacuum; these liners were introduced into the pressure bomb as previously described.[7,8]

The vapor pressures were determined on two separate loadings in the same dead-weight piston apparatus used for the compressibility measurements at different relative values of vapor and liquid volume; they were found essentially independent of the relative volumes over a large range. This behavior indicated the sample to be of reasonably high purity.

The decomposition rate at temperatures up to 225° is extremely small as indicated by the reproducibility of the pressure readings on returning to a given specific volume from a higher or lower one. However, at 250°, the decomposition rate becomes sufficiently rapid to make reproducible readings impossible and vapor pressure readings were no longer independent of the relative vapor-liquid volumes.

The Material Used.—The 1,2-dichloro-1,1-difluoroethane sample was obtained from Halogen Chemicals, Inc., of Columbia, South Carolina. It was repurified by means of fractional distillation using a 1.5 meter, packed column. The middle portion was collected for use and had a constant boiling point of 46.64°, determined with a thermometer calibrated by the National Bureau of Standards (this middle-cut distillation temperature remained constant for a five-hour period). The value of $n^{20}\text{D}$ was found to 1.3619_6. Henne and Hubbard's values for the boiling point and $n^{20}\text{D}$ were, respectively, 46.8° and 1.36193.[4]

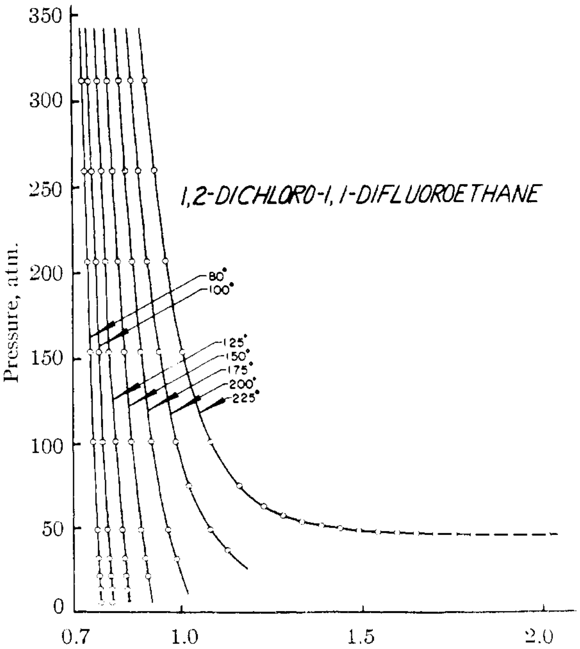

Fig. 1.—Isotherms of 1,2-dichloro-1,1-difluoroethane.

This middle portion of this fraction was distilled into a glass reservoir under a vacuum, from whence it was distilled at very low temperatures under vacuum into the various calibrated glass liners for the pressure bomb.

Results and Discussion

The vapor pressures are presented in Table I and the compressibilities in Table II and Fig. 1. The critical temperature has been calculated by

TABLE I

EXPERIMENTAL VAPOR PRESSURES OF 1,2-DICHLORO-1,1-DIFLUOROETHANE

Temp. (°C.)	Vapor pressure (atm.)	Temp. (°C.)	Vapor pressure (atm.)
110	5.973	170	19.493
120	7.460	180	23.000
130	9.205	190	27.010
140	11.261	200	31.514
150	13.639	210	36.643
160	16.386	220	43.576

TABLE II

COMPRESSIBILITY OF LIQUID AND GASEOUS 1,2-DICHLORO-1,1-DIFLUOROETHANE

Specific vol. (ml./g.)	Total pressure (atm.)
80° Isotherm	
0.7759	5.602
.7736	13.504
.7718	21.399
.7695	31.903
.7662	49.010
.7553	101.514
.7473	154.061
.7401	206.692
.7331	259.359
.7272	311.801
100° isotherm	
0.8063	5.598
.8033	13.500
.8013	21.397
.7984	31.901
.7942	49.008
.7813	101.513
.7710	154.058
.7621	206.689
.7533	259.377
.7457	311.799
125° isotherm	
0.8494	13.500
.8460	21.397
.8414	31.901
.8350	49.008
.8165	101.513
.7982	154.058
.7909	206.689
.7805	259.357
.7710	311.799
150° isotherm	
0.9078	21.395
.8996	31.899
.8882	49.006
.8606	101.509
.8405	154.056
.8246	206.687
.8107	259.353
.7993	311.795
175° isotherm	
0.9862	31.894
.9627	49.001
.9167	101.503
.8865	154.048
.8642	206.678
.8466	259.344
.8314	311.786
200° isotherm	
1.1293	37.145
1.0811	48.988
1.0209	75.229
0.9853	101.489
.9387	154.035
.9072	206.663
.8834	259.330
.8643	311.771
225° isotherm	
2.0149	45.578
1.9626	45.667
1.9101	45.800
1.8567	46.008
1.8053	46.181
1.7528	46.380
1.7005	46.618
1.6480	46.926
1.5956	47.296
1.5433	47.903
1.4909	48.687
1.4386	49.783
1.3863	51.367
1.3340	53.826
1.2819	57.425
1.2301	62.906
1.1612	75.209
1.0828	101.466
1.0046	154.009
0.9580	206.637
0.9279	259.302
0.9037	311.744

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[7] E. A. Kelso and W. A. Felsing, THIS JOURNAL, **62**, 3132 (1940); *Ind. Eng. Chem.*, **34**, 161 (1942).

[8] M. L. Deviney, Jr., M.A. Thesis, University of Texas, January, 1952.

the method of Meissner and Redding[9] to be 222.0°. This temperature must be quite near the *true* critical temperature, since vapor pressure measurements at 220° were exceedingly difficult to make. For the temperature range 110–210°, log *p* is approximately a linear function of the reciprocal of the absolute temperature; the value at 220° was not included in the derivation of the relationship

$$\log p\ (\text{atm.}) = 4.3609386 - \frac{1409.0428}{(T + 273.16)} + 0.000244348(T + 273.16)$$

where T is in °C.

The maximum deviation between the experimental vapor pressure and the vapor pressures calculated by the above equation is 0.30%; this equation reproduces 9 of the 11 experimental points to 0.15% or less.

The compressibility values are believed to be accurate to within 0.1 to 0.2%. The decomposition of 1,2-difluoro-1,1-dichloroethane proceeded slowly enough even at the highest temperatures to provide accurate P–V–T data; the vapor pressure values are changed more by a slight decomposition than are the compressibility values.

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KINGSVILLE, TEXAS

[9] H. P. Meissner and E. M. Redding, *Ind. Eng. Chem.*, **34**, 521 (1942).

[CONTRIBUTION FROM THE DIVISION OF APPLIED CHEMISTRY, NATIONAL RESEARCH COUNCIL (CANADA)]

Cationic Polymerization of α-Methylstyrene

BY D. J. WORSFOLD AND S. BYWATER

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The kinetics of polymerization of α-methylstyrene with a boron trifluoride–ether–water complex have been studied. The reaction rate has been found to be governed by the expression $-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_1[\mathrm{c}][\mathrm{M}]\ (2 + k_p[\mathrm{M}]/k_t)$ and the degree of polymerization by $\overline{\mathrm{DP}} = 2 + k_p[\mathrm{M}]/k_t$. The nature of the termination step has been investigated. The cause of the low degree of polymerization has been identified as a low propagation rate compared with the termination reaction.

The heat of polymerization of α-methylstyrene is known to be only of the order of 8 kcal. This would lead to the conclusion that the ceiling temperature for polymerization, as defined by Dainton and Ivin,[1] would be somewhat above room temperature. It is known, moreover, that the radical polymerization of this monomer is very difficult and at ambient temperature only low molecular weight polymers are produced with the Friedel–Crafts type of catalysts. It would seem desirable therefore to carry out kinetic measurements at lower temperatures using cationic catalysis whereby rather higher molecular weight polymers are formed in order to determine more certainly the cause of the low degree of polymerization. The two principal previous studies of this reaction, one by Jordan and Mathieson,[2] using aluminum chloride in carbon tetrachloride solution and one by Dainton and Tomlinson[3] using stannic chloride in ethyl chloride solution, are so contradictory that the study of a third system would seem worthwhile. The system chosen was boron trifluoride etherate in the presence of excess water and diethyl ether in ethylene chloride solution. The kinetics were found to follow very closely the mechanism proposed by Dainton and Tomlinson for their system.

Experimental

Materials.—Ethylene chloride was stirred with concentrated sulfuric acid for four days, washed, dried and distilled from aluminum chloride, and after a final wash was fractionally distilled over phosphoric oxide. The product was degassed and stored under vacuum.

α-Methylstyrene was fractionally distilled under vacuum, and stored under vacuum. Boron trifluoride was sublimed under vacuum and stored at liquid nitrogen temperature. Diethyl ether was distilled from sodium wire and then from phosphorus pentoxide into a trap on the vacuum system.

Procedure.—Since it has been reported that cationic polymerizations are rendered more reproducible by having a fair excess of water present, the concentration of water in practically all runs was at such a level that a very limited exposure to the atmosphere was considered permissible in that the water pick up would be negligible compared to the added water.

Solutions of monomer and water in ethylene chloride and boron trifluoride and ether in ethylene chloride, were prepared under vacuum, and blanketed with dry nitrogen. The reaction was started by pipetting a little of the catalyst solution into the monomer solution.

Samples were siphoned from the reaction vessel at intervals and the residual monomer estimated with mercuric acetate in methanol solution.[4] The initial rates were found from the first 10% or less of the reaction; rates given are in units of moles/l./minute. The molecular weights were determined after 10% reaction using the viscosity relationship, for benzene solution at 30°.

$$[\eta]_{\mathrm{sp0}}/c = 0.0105 + 1.787 \times 10^{-5}\ M$$

obtained from cryoscopic measurements on unfractionated polymer samples.

Results

The effect of temperature on the initial rates and degree of polymerization at various monomer concentrations was investigated at five temperatures between +20° and −20°.

At +20° the initial rates are very nearly dependent on the first power of the monomer concentration (Fig. 1), but at the lower temperatures the order increases and the whole series is adequately described by the expression

$$\text{Initial rate} = K_1[\mathrm{M}](C + K_2[\mathrm{M}])$$

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[1] F. S. Dainton and K. J. Ivin, *Nature*, **162**, 705 (1948).

[2] D. O. Jordan and A. R. Mathieson, *J. Chem. Soc.*, 2354 (1952).

[3] F. S. Dainton and R. H. Tomlinson, *ibid.*, 151 (1953).

[4] R. W. Martin, *Anal. Chem.*, **21**, 921 (1949).